치의과학 박사학위논문

Bonding Effect of Universal Adhesives as the Surface Treatment Agents to Lithium Disilicate

리튬 다이실리케이트의 표면 처리 시 유니버설 접착제의 접착효과

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Abstract

Bonding Effect of Universal Adhesives as the Surface Treatment Agents to Lithium Disilicate

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Objective

This study evaluated the influence of universal adhesives (UAs), as surface treatment agents to lithium disilicate (LS2), on the bond strength of two resin cements using a microshear bond strength test.

Materials and Methods

Amine-free resin cements such as Nexus3 (NX3, Kerr) and RelyX ultimate (RXU, 3M ESPE) were used.

A total of 72 rectangular plates LS2 ceramic specimens (IPS e.max CAD, Ivoclar Vivadent) were fabricated. The surfaces were treated as follow:

For NX3, Group A, adhesive (Ad, Porcelain Bonding Resin, Bisco Inc.); Group B, silane (S, Bis-Silane, Bisco Inc.) and Ad; Group C, 5% hydrofluoric acid (HF, Ceramic Etching Gel, Ivoclar Vivadent), S and Ad; Group D, Single Bond

Universal (SBU, 3M ESPE); Group E, HF and SBU.

For RXU, Group I, Ad; Group II, HF, S and Ad; Group III, HF and SBU; Group IV, HF and All Bond Universal (ABU, Bisco Inc.).

The Prefabricated composite resin (Filtek Z250, 3M ESPE) cylinders (n = 40) of 0.8 mm in a diameter were placed before light polymerization. Bonded specimens were stored in water for 24 hours and half of specimens (n = 20) underwent a 10,000-cycle thermocycling process prior to the μSBS testing. The data of each experiment were analyzed using multivariate analysis of variance with Tukey HSD post hoc tests ($p < 0.05$). Comparing the effect of resin cements, the data were analyzed using three-way analysis of variance ($p < 0.05$).

Results

For NX3, bond strength varied significantly among the groups ($p < 0.05$), except for Groups A and D. Group C showed the highest initial bond strength (23.88 MPa), followed by Group E (19.50 MPa), Group B (9.23 MPa), Group D (2.04 MPa) and Group A (1.80 MPa). Thermocycling significantly reduced bond strength in Groups B, C, and E ($p < 0.05$). Bond strength of Group C was the highest regardless of the storage conditions ($p < 0.05$).

For RXU, before thermocycling, the bond strength of Group III (23.50 MPa) was similar to that of Group II (22.78 MPa) ($p > 0.05$), and was higher than that of Group IV (18.59 MPa) ($p < 0.05$). Bond strength of Group I, negative control, was significantly lower than that of other groups ($p < 0.05$). After thermocycling, the bond strengths significantly decreased in all groups ($p < 0.05$) and Group II showed the highest bond strength value ($p < 0.05$).

Comparing to the effect of resin cements, after thermocycling, the bond strength

of RXU was higher than that of NX3 when the surface was treated with HF and SBU ($p < 0.05$).

Conclusions

Surface treatment using UA could not form effective bond of resin cement to LS2. After thermocycling, two UAs could not durably bond to LS2 compared to a separated use of silane and adhesive, though the surface was treated with HF.

Keywords: Lithium disilicate, Universal adhesive, Microshear bond strength, Resin cement, Silane, Thermocycling

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Contents

I. Introduction

All-ceramic restorations have gained popularity because of their biocompatibility and translucency as well as good esthetics.[1,2] The chosen material for all-ceramic restorations has shifted from pressed ceramic to monolithic ceramic to improve the mechanical properties. Lithium disilicate (LS2), monolithic ceramic, is popular because of good esthetics and better chipping fracture resistance relative to non-monolithic materials such as porcelain-veneered zirconia.[3] It also has higher strength than other ceramic materials such as leucite glass and metal ceramics.[4]

The clinical outcomes of ceramic restoration do not depend only on the properties of the material, but also on the resin-ceramic bond. Strong and durable resin bonding increases retention,[5,6] improves marginal adaptation,[7,8] reduces microleakage[8,9] and enhances fracture resistance.[10] This resin-ceramic bond is created through micromechanical retention and chemical bonding to a silica-based ceramic surface.[11,12] To produce micromechanical retention, the surface is prepared by airborne-particle abrasion and/or etching with hydrofluoric acid (HF). However, airborne-particle abrasion is not recommended due to a significant reduction in the flexural strength of IPS e.max CAD (Ivoclar Vivadent, Schaan, Liechtenstein).[13] HF etching dissolves the glass phase from the matrix, thus creating micro-undercuts and increasing the surface area.[14] Chemical bonding between the resin-ceramic surfaces can be achieved by using a silane coupling agent. Silane is a bifunctional molecule that promotes adhesion via covalent bonds with hydroxyl (OH) groups on the ceramic surface.[15] One functional group can react with the inorganic ceramic surface and the other is a methacrylate group capable of reacting with an organic resin matrix.[16]

Recent trend in adhesive dentistry is to simplify bonding procedures by reducing the application steps.[17] Accordingly, many manufacturers have introduced new single-bottle adhesives called 'universal' or 'multi-mode' adhesives (UAs). They contain many ingredients, such as bisphenol A glycidyl methacrylate (Bis-GMA), 2-hydroxyethyl methacrylate (HEMA), 10-methacryloyloxydecyl dihydrogen phosphate (MDP), and/or silane. However, MDP and silane are usually not included in conventional ceramic adhesives. As MDP is a versatile amphiphilic functional monomer, it is the most important component in UAs for practical use. MDP has the potential to bond chemically to metals,[18] zirconia,[19] and tooth tissue.[20] Furthermore, it possesses the 'ideal' bonding agent property, that the polar phosphate group of the functional monomer is initially hydrophilic, but MDP becomes more hydrophobic once polymerized.[21] Several studies investigated the bond strength of UAs applied on several materials such as enamel,[22] dentin,[23] zirconia,[24,25] and ceramics.[10,26] The manufacturer-proposed UAs containing silane could promote bonding to glass ceramics or resin composites without additional priming procedures. Previous study suggested UAs might have potential to use in adhesive dentistry.[27] Other studies have suggested silane have to be applied to lithium disilicate when UAs was applied.[28,29] However, little is known regarding the bonding behavior of UAs to LS2 with thermocycling compared with a separate use of silane and adhesive.

The purpose of our current study was to investigate the effects of UAs on the bonding of resin cement to LS2 ceramic using the microshear bond strength (μSBS) test. The null hypotheses tested were: (1) silane-containing UA does not increase the bond strength compared with a separate use of silane and adhesive; and (2) thermocycling does not affect μSBS when UAs are applied.

II. Review of Literature

Ceramics are formed from nonmetallic, inorganic material containing compounds of oxygen with one or more metallic or semi-metallic elements, such as sodium, potassium, calcium, magnesium, aluminum, silicon, zirconium and so on.[30] Porcelain refers to a specific ceramic material composed mainly of feldspars (potassium and sodium aluminosilicates), quartz (silica), and kaolin (hydrated aluminosilicate) fired at high temperatures.[31]

1. History of Dental Ceramics

The first use of ceramics was for fabricating a complete denture for Duchateau in 1774. Giuseppangelo Fonzi, an Italian dentist, advanced the versatility of ceramics by firing denture teeth, each including a platinum pin or frame in 1808.[32] In England, improved platinum tooth were developed by Ash in 1837. Land introduced the first feldspathic porcelain as the porcelain jacket crown in 1903.[33] This crown provided esthetics, but had low flexural strength (65 MPa).[34] The first commercial porcelain was introduced by VITA Zahnfabrik about 1963. McLean added alumina (Al_2O_3) to feldspathic porcelain to improve mechanical properties by a mechanism called "dispersion strengthening" in 1965.[35,36] Because this aluminous core was opaque, feldspathic porcelain veneer was required to achieve esthetics. The flexural strength of the aluminous core (128.7 MPa) was not strong enough to resist posterior occlusal force.[37] The use of the aluminous porcelain crowns was restricted at maxillary anterior teeth.[35]

Metal-ceramic crowns are more durable and fracture-resistance than all-ceramic crowns. However, disadvantages of metal-ceramic crowns are esthetics as well as

biocompatibility. All-ceramic systems have been tremendously improved in last three decades to response to patients' demands. The commercial available castable glass ceramic, Dicor (Dentsply International, York, PA, USA), was introduced and was improved by controlled crystallization in 1984.[38] After then, numerous types of glass ceramic were made containing of leucite (IPS Empress [Ivoclar Vivadent]) or LS2 (IPS Empress 2 [Ivoclar Vivadent], IPS e.max [Ivoclar Vivadent]).[39] Furthermore other processing methods were developed such as glass infiltration, hot-isostatic pressing, and computer-aided design/computer-aided manufacturing (CAD/CAM) milling.

2. Lithium Disilicate (LS2)

LS2 glass ceramic material is introduced by Ivoclar Vivadent for use in all-ceramic restorations and is composed of quarts, lithium dioxide, phosphorus oxide, alumia, and potassium oxide.

IPS Empress 2 is the most representative pressable ceramic and contains about 60 wt% LS2.[40] Its flexural strength is 312 to 407 MPa and fracture toughness is 3.3 $MPa \cdot m^{1/2}$.[35,37] It could fabricate three-unit fixed partial dentures from anterior teeth to the second premolar. However, it was designed as a core material because it is more opaque than the leucite-based glass ceramic. Although the fracture toughness of core ceramics is high, veneers with low strength glass ceramics were susceptible to chipping.[41]

IPS e.max was introduced in 2005. The mechanical properties are improved because it has high crystal contents (70% crystal phase).[42] Its flexural strength is 360 to 400 MPa.[43] This material refracts light naturally and has chameleon effect due to high translucency.[4,43]

The pressable LS2 (IPS e.max Press [Ivoclar Vivadent]) is available as an ingot and is processed in using lost-wax hot pressing technique. Its microstructure consists of 70% needle-like LS2 crystals in a glassy matrix. These crystals are 3 to 6 μm in length. While machinable LS2 blocks (IPS e.max CAD) are provided in precrystallized state with blue-violet color to be milled easily. The final crystallization occurs after milling the blocks by means of CAD/CAM technology. This crystallization process results in a glass ceramic with 70 vol% fine-grain LS2 crystals which range in 0.2 to 1.0 μm in length.[43] Machinable ceramic is less affected by corrosion and is higher flexural strength and higher micro-hardness compared to pressable ceramic.[44] The prefabricated CAD blocks have superior mechanical properties as they are homogeneous with few flaws.[45] This high strength ceramic could be applied versatilely such as single crowns in both anterior and posterior teeth as monolithic ceramic.

3. Bonding to Ceramic

(1) Surface Treatment

To achieve mechanical bonding to ceramic surface, the surface is prepared by grinding with a diamond rotary instrument, airborne-particle abrasion and/or etching with HF. Grinding with bur is non-consistent and arbitrary. Airborne-particle abrasion is roughen the ceramic surface with alumina particles (25-50 μm) in pressurized air (0.28 MPa) and creates micromechanical undercut.[46,47] It is suitable treatment with industrial application. Furthermore, Borges *et al*.[48] showed that airborne-particle abrasion with 50 μm alumina increased surface irregularities of leucite-reinforced ceramics and LS2-reinforced ceramic. However, it is not recommended because of reduction in the strength of LS2.[13]

HF is aqueous solution of hydrogen fluoride. The ceramic material that contains a glass phase (silica-based feldspathic, leucite-reinforced, or LS2-reinforced ceramics) can be etched with HF. It can dissolve the ceramic glass phase from the matrix by reacting with silicon dioxide. The reaction is shown as:

$$SiO_2(s) + 2(HF)_2(l) \rightarrow SiF_4(l) + 2H_2O(l) \quad (1)$$

$$SiF_4(l) + (HF)_2(l) \rightarrow [SiF_6]^{2-}(aq) + 2H^+(aq) \quad (2)$$

$$[SiF_6]^{2-}(aq) + 2H^+(aq) \rightarrow H_2SiF_6(l) \quad (3)$$

Finally hexafluorosilicic acid is formed and can be rinsed off with water. Therefore, both roughness and the surface area of ceramics are increased and the HF etching also creates micro-undercut.[14,49]

Various studies reported HF etching increased in bond strength between silica-based ceramics and resin cement.[50-53] Some studies were tried to examine the effect of concentration and duration of HF etching on the bond strength.[54-58] It was shown, where etching times (10 seconds, 20 seconds, 40 seconds, 1 minute, and 2 minutes) were examined on leucite-reinforced glass ceramic, that increased etching periods generally decreased the bond strength when it treated with both 10% HF and silane.[55] Chen *et al*.[54] evaluated the effect of different HF (5%) etching duration on feldspathic ceramic. The highest bond strength showed when the ceramic surface was etched during 2 minutes, and the shear bond strength was decreased when the etching time beyond the period. It was reported that the bond strength with 16.8% HF etching for 30 seconds was lower than that of 16.8% HF etching for 5

seconds.[56] This could be explained by over-etching of ceramic surface and adversely affecting the bond strength. The higher concentration of HF both LS2- and leucite-reinforced ceramic surfaces was etched with, the higher bond strength was.[58]

Previous studies demonstrated that the strength of ceramic materials can be altered by HF etching. Hooshmand *et al.*[59] reported that 9% HF etching for 2 minutes reduced the biaxial flexural strength of IPS Empress and IPS Empress 2. Other study reported that flexural strength of LS2 after 90 seconds of etching with 4.9% HF was significantly reduced.[60,61] Therefore, the manufacturer recommends that the surface of IPS e.max CAD was etched for 20 seconds with 4.9% HF.[62] Other manufacturers of HF etching gels (Porcelain etchant [9.5% HF], Bisco Inc., Schaumburg, IL, USA; Porcelain etch [9% HF], Ultradent Inc., South Jordan, UT, USA) recommend etching times of 90 seconds.[63]

Both HF etching and airborne-particle abrasion are not effective on the surface of glass-infiltrated aluminum oxide ceramic and zirconium-reinforced ceramic.[48] Clinician should consider the type of ceramic being used before surface preparation.

(2) Silanization

Silane is a bifunctional molecule; One functional group can react with the inorganic ceramic surface and the other is a methacrylate group capable of reacting with an organic resin matrix.[16] Silanization could reduce the contact angle and thus increase wettability of the ceramic.

The silane usually exist in a less reactive alkoxide (-Si-OR) form in solution, which is non-functional silane.[64] With an acidic catalyst, the alkoxy groups react with water to form reactive silanol groups. This hydrolysis reaction can be simply

presented:

$$R\text{-}Si\text{-}(OR')_3 + 3H_2O \rightarrow R\text{-}Si\text{-}(OH)_3 + 3R'OH \quad (4)$$

When the silane is applied on ceramic, silanol groups of silane react with hydroxyl groups of the ceramic surface while liberating water molecules to form siloxane (Si-O-Si) covalent bonds. This reaction is enhanced by acidic condition and warm air drying.[65,66] Drying with warm is accelerated evaporation of water, alcohol and other solvent, and thus equilibrium of silanization reaction is broken and is shifted forward.

Widely used silane agents are 3-Methacryloxypropyltrimethoxysilane, 3-Acryloxypropyl trimethoxysilane, 10-Methacryloxydecyltrimethoxysilane, and 3-(3-Methoxy-4-methacryloyloxyphenyl) propyltrimethoxysilane.

Commercially silane products are available in either one component prehydrolyzed silane or two-liquid with unhydrolyzed silane and acid activator. Prehydrolyzed silane solutions are mixed silane coupling agent, solvent and an acid together. Therefore, its stability could be insufficient and its shelf life is limited. Kato *et al*.[67] reported that two- or three-component silanes achieved a durable bond to porcelain restorations compared to a prehydrolyzed silane.

4. Universal Adhesives (UAs)

As dental materials and adhesive dentistry have been explosively developed since late 20th century, numerous products have been released to simplify clinical steps and to save chair time. Clinicians have used primers and adhesives to bond a variety of restoration materials to tooth until a few year ago. Manufacturers were

rushing to launch new single-bottle, no-mix adhesives. They are applied using a total-etch, selective-etch or self-etch technique on enamel and dentin. While dentin etched with phosphoric acid showed longer resin tag and thicker hybrid layer than unetched dentin, microtensile bond strength (μTBS) did not affected by the addition of an etching.[68] Additionally, UAs are capable of bonding direct and indirect restorations. They contain MDP for metals[18] and zirconia[19] and/or silane for composites and various silica-based ceramics.

III. Materials and Methods

1. Specimen Preparation

Seventy-two rectangular plates (12 mm × 14 mm × 5 mm) of IPS e.max CAD blocks were fabricated (Table 1). The blocks were sintered in a furnace (Horizon Press, Shenpaz, Migdal HaEmek, Israel) according to the manufacturer's instructions (Table 2). After cooling, each specimen was embedded into an acrylic resin block. To establish a uniform surface, the LS2 surfaces were sequentially polished with 120-, 220- and 500-grit silicon carbide paper using an automatic polishing machine (Rotopol-V, Struers, Ballerup, Denmark) under water cooling (clockwise rotation, 120 N for 1 minute with 120 grit, 120 N for 20 seconds with 220 grit, and 30 N for 10 seconds with 500 grit). The specimens were treated with 10% citric acid,[69] were cleaned in an ultrasonic water bath for 10 minutes to remove the smear layer, and then were dried under vacuum for 24 hours.

2. Surface Treatment of LS2 Blocks and Cementation

Two amine-free resin cements were used in this study.

2-1. Nexus3 (NX3)

Forty ceramic specimens were randomly divided into five groups (Figure 1a), that is eight ceramic specimens per group. The LS2 surface of each specimen was treated as follows:

Group A (Ad, control): an adhesive that did not contain silane (Ad, Porcelain Bonding Resin, Bisco Inc.) was applied with a microbrush.

Group B (S+Ad): silane (S, Bis-Silane, Bisco Inc.) was applied and air-dried,

followed by application of Ad as above.

Group C (HF+S+Ad): 5% HF (Ceramic Etching Gel, Ivoclar Vivadent) was applied for 20 seconds, rinsed with distilled water for 1 minute and air-dried. Then, S and Ad were applied in the same manner as in Group B.

Group D (SBU): The surface was treated with Single Bond Universal (SBU, 3M ESPE, St. Paul, MN, USA) and agitated via scrubbing with a microbrush for 20 seconds. It was then gently air-dried for 5 seconds.

Group E (HF+SBU): 5% HF was applied for 20 seconds, rinsed with distilled water for 1 minute and air-dried. Then, the surface was treated with SBU in the same manner as in Group D.

A dual-cure resin cement that did not contain amine (NX3, shade clear; Kerr, Orange, CA, USA) was applied and 5 pre-cured composite resin (Filtek Z250, 3M ESPE) cylinders (n = 40) with a diameter of 0.8 mm were placed on eight treated ceramic surfaces in each group under a fixed load of 0.4 N. After excess cement was removed with microbrushes, the resin cement was light-cured for 40 seconds with an LED light-curing machine at wavelengths of 430-490 nm (Be Lite, B&L Biotech, Ansan, Korea).

2-2. RelyX ultimate (RXU)

Thirty two ceramic specimens were randomly divided into four groups (Figure 1b), that is eight ceramic specimens per group. The LS2 surface of each specimen was treated as follows:

Group I (Ad, control): Ad was applied with a microbrush.

Group II (HF+S+Ad): 5% HF was applied for 20 seconds, rinsed with distilled water for 1 minute and air-dried. Then, S and Ad were applied in the same

manner as in Group B.

Group III (HF+SBU): 5% HF was applied for 20 seconds, rinsed with distilled water for 1 minute and air-dried. Then, the surface was treated with SBU and agitated via scrubbing with a microbrush for 20 seconds. It was then gently air-dried for 5 seconds.

Group IV (HF+ABU): 5% HF was applied for 20 seconds, rinsed with distilled water for 1 minute and air-dried. Then, the surface was treated with one coat of All Bond Universal (ABU, Bisco Inc.) and air dry. It was then light-cured for 10 seconds.

A dual-cure resin cement that did not contain amine (RXU, shade transparent; 3M ESPE) was applied and 5 pre-cured composite resin (Filtek Z250, 3M ESPE) cylinders (n = 40) with a diameter of 0.8 mm were placed on eight treated ceramic surfaces in each group under a fixed load of 0.4 N. After excess cement was removed with microbrushes, the resin cement was light-cured for 40 seconds with an LED light-curing machine at wavelengths of 430-490 nm (Be Lite).

3. Microshear Bond Strength Testing

All specimens were stored in distilled water at 37℃ for 24 hours and were divided randomly into two subgroups. Half (n = 20) were subjected to μSBS testing, and the remainder (n = 20) were thermocycled for 10,000 thermal cycles with a dwell time of 24 seconds and a transfer time of 6 seconds between 5℃ and 55℃ water baths and subjected to μSBS testing.

The specimens were mounted in the jig of a universal testing machine (UTM, LF Plus, Lloyd Instruments Ltd, Fareham Hampshire, England). A wire 0.2 mm in diameter was looped around the resin composite cylinder as closely as possible to

the bonded interface. The shear force was applied at a cross-head speed of 0.5 mm/min until failure occurred. If premature failure occurred before bond strength testing, the bond strength was recorded as 0 MPa.

4. Failure Analysis

After μSBS testing, the fractured interfaces of the specimens were observed using a stereomicroscope (SZ-PT, Olympus Co, Tokyo, Japan) at 40× magnification to determine the failure mode. The failure mode was classified as 'adhesive failure' when it occurred between the ceramic and the resin cement, 'cohesive failure' when it occurred within the ceramic or resin and 'mixed failure' when a combination of adhesive and cohesive failures occurred. The representative fractured surface were examined in a field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi High technologies Co, Tokyo, Japan) operated at 15 kV.

5. Microscopic Observation of Bonded Interfaces

To observe the bonded interfaces among the LS2 ceramic, adhesive, and resin cement, 3 mm × 5 mm × 14 mm IPS e.max CAD stick specimens (n = 4) were prepared. The ceramic surfaces were treated according to the procedures for each group using NX3. The resin cement (NX3, Kerr) was applied and light-cured for 40 seconds. All specimens were stored in water for 24 hours, and half were subjected to 10,000 cycles of thermocycling. To observe the bonding quality, the middle point of each stick specimen was fractured perpendicular to adhesive interface in compression mode with a UTM. The fractured surfaces of the sticks were observed by FE-SEM.

6. Statistical Analysis

Bond strength data of each resin cement were statistically analyzed using multivariate analysis of variance (MANOVA) with statistical software (SPSS version 18.0, SPSS Inc., Chicago, IL, USA). Multiple comparisons were performed using the Tukey HSD test, where a *p*-value less than 0.05 was considered statistically significant. To compare the effect of resin cements, the groups were classified according to same surface treatments (Groups A and I, Groups C and II, Groups E and III). The bond strength data were analyzed using three-way analysis of variance (ANOVA) with the significance level defined as $\alpha = 0.05$.

In addition, a Weibull analysis of the μSBS data was also carries out. The Weibull parameters, such as the Weibull modulus (m) and the characteristic bond strength (σ_θ), were obtained to compare the distribution of the failure probability of each group among the surface treatments and between the testing conditions; before and after thermocycling.

IV. Results

For NX3, the mean bond strength values and standard deviation are presented in Table 3. Before thermocycling, the bond strength of Group A (1.80 MPa) was the lowest. The bond strength of Group D (2.04 MPa) was similar to that of Group A and was lower than that of Groups B (9.23 MPa) ($p < 0.05$). Evaluating the effect of HF etching, Groups C (23.88 MPa) and E (19.50 MPa) showed higher bond strength than other groups ($p < 0.05$). The mean shear bond strength for Group C was significantly higher than that of Group E ($p < 0.05$),

During the thermocycling procedure, all specimens of Groups A and D were spontaneously debonded, which were not treated with HF. Although the ceramic surface of Group B was also not treated with HF, the bond strength of Group B was 3.03 MPa after thermocycling. After thermocycling, the bond strengths decreased in Groups B, C and E ($p < 0.05$). Group C showed the highest bond strength regardless of the testing conditions ($p < 0.05$).

Weibull analysis data are given in Table 4. The Weibull curves, shown in Figures 2a and 2b, have shear stress plotted on the x-axis and probability of failure on the y-axis. After 24-hour water storage, the Weibull moduli for HF and/or silane treated groups (Groups B, C, and E) were higher than for the other groups. Both Groups C (HF+S+Ad) and E (HF+SBU) had higher characteristic bond strength (σ_θ) values as shown by the position of the Weibull curves at higher stress levels (Figure 2a). While the *m* increased in Group C after thermocycling, the *m*'s decreased in Groups B and E. After thermocycling, all Weibull curves shifted to left. In Group E, the amount of shifts in the graph was the largest.

The distribution of failure modes after μSBS testing is presented in Figure 3a.

The mode of failure was all adhesive failures in Groups A and D. However, cohesive and/or mixed failures (15 to 35%) occurred in the HF-treated groups (Groups C and E). After thermocycling, 100% of the failures were adhesive in Group B, whereas mixed failures (35 and 10%) occurred in Groups C and E. Group C had fewer adhesive failures than Group E did.

Figure 4 shows representative SEM images of LS2 surface after μSBS tests.

While the specimens were being processed for microscopic observation of the bonded interfaces, all specimens spontaneously debonded in Groups A and D before thermocycling and in Groups B and E during thermocycling. There was no gap between the ceramic and adhesive in Group C before or after thermocycling (Figure 5b and 5d) compared to Groups B and E before thermocycling (Figure 5a and 5c).

For RXU, the mean bond strength values and standard deviation are listed in Table 5. Before thermocycling, the bond strength of Group I (2.44 MPa) was the lowest, similar to Group A (Figure 6a) as negative control. Evaluating the bonding effect of UAs, Group III (23.50 MPa) showed similar bond strength to Group II (22.78 MPa) ($p > 0.05$), and the bond strength of Group IV (18.59 MPa) was lower than that of Groups II and III ($p < 0.05$). During the thermocycling procedure, all specimens of Groups I were spontaneously debonded which was not applied HF. After thermocycling, the bond strengths decreased in Groups II, III and IV ($p < 0.05$). Group II showed the highest bond strength ($p < 0.05$).

Table 6 shows the Weibull analysis data with their corresponding confidence intervals. The Weibull curves are also shown in Figures 2c and 2d. HF-treated groups showed higher m than non HF-treated group (Group I). Before thermocycling, characteristic bond strength of HF-treated groups is also higher

than Group I, as shown by the right-shifted Weibull curves of HF-treated groups. After thermocycling, the *m* decreased in both Groups III and IV. However, the *m's* of Group II were similar between before and after thermocycling. Characteristic bond strength (σ_θ) decreased in all groups after thermocycling. The Weibull curve of Group II was located right-side in Figure 2d.

The distribution of failure modes after μSBS testing is presented in Figure 3b. After 24-hour water storage, Group III showed mixed failure (5%), but other groups were all adhesive failure. After thermocycling, mixed failure (5%) was occurred in Group II and the cohesive failures of resin (10%) were observed in Group III.

Comparing the bond strength between resin cements, the result are shown in Figure 6. Three-way ANOVA showed that bond strength was not significantly influenced by cement ($p = 0.052$), by the interaction of testing conditions and cement ($p = 0.684$), by the interaction of surface treatment and cement ($p = 0.287$), and by all these three factors ($p = 0.307$). Significant statistical interaction was found between surface treatment and testing condition ($p < 0.001$). Before thermocycling, no statistically significant difference was found in bond strength values between NX3 and RXU (Groups A and I, C and II, E and III) ($p > 0.05$). After thermocycling, the bond strength was not statistically different when the ceramic surface was treated with only Ad (Groups A and I) and with HF, S and Ad (Groups C and II). However, the mean bond strength using RXU (Group III) was higher than that of using NX 3 (Group E) when surface was treated with HF and SBU ($p < 0.05$).

V. Discussion

The aim of this study was to examine the bonding performance of UAs to LS2 compared to a separated use of silane and adhesive using μSBS testing. The result after 24-hour water storage of NX3 indicated that SBU without HF etching provided lower bond strength values than the separate use of silane and hydrophobic adhesives and similar bond strength to negative control treated with hydrophobic adhesive only. When the surface treated with SBU only, all resin cylinders were debonded during thermocycling. The bond strength treating with HF and SBU was lower than that treated with HF, silane and adhesive in both testing conditions of NX3 and after thermocycling of RXU. Therefore the first null hypothesis of the current study was accepted. After thermocycling, bond strength values were significantly decreased compared to baseline values in Groups D, E, III and IV (Tables 3 and 5). The results indicated that we could reject the second hypothesis.

Several testing methods were applied to evaluate the bond strength between different materials, such as shear bond strength (SBS), tensile bond strength (TBS), μSBS, and μTBS tests. The larger the bonding area is, the higher the likelihood of a flaw being present and the lower the bond strength.[70] Either μSBS or μTBS tests are the most common approach. The μTBS test requires a uniform stress distribution during loading.[71] However, it is difficult to fabricate microbeam specimens with sintered IPS e.max CAD blocks without damaging the bonded interface. Conversely, μSBS specimens are pre-stressed prior to testing only by mold removal.[72] Therefore, in this study, the μSBS test method could be used, because not only is it a simple and reproducible procedure,[73] but it also permits

efficient screening of adhesive systems.[70]

UAs have low pHs due to a phosphate monomer, MDP. According to technical information provided by manufacturers, the pHs of SBU and ABU are 2.7 and 3.2, respectively. When it is mixed with self-cure or dual-cure resin cements, an acid-base reaction occurs between acidic components (MDP) of UAs and an aromatic tertiary amine which is the activator of chemical polymerization in resin cements. The consequence of this reaction is a lack of polymerization at the adhesive-cement interface. Therefore, the manufacturers of UAs (pH < 3) recommend mixing it with a separate activator if a self-cure or dual-cure resin cement is used,[21] or to use it with an amine-free dual-cure resin cement. When UAs are used with their activators, it is obtained in two different bottles. This does not have any advantages compared to the separate silane and adhesive system, like Groups C and II. Simpler clinical process was chosen, using the amine-free dual-cure resin cements (NX3 and RXU).

In this study, the application of SBU alone showed similar bond strength to Group A and lower bond strength than Group B. All resin cylinders of Group D were debonded during thermocycling, but those of Group B were not. Furthermore, the lower bond strengths obtained by HF and SBU, compared with the HF, silane and adhesive using NX3 (Table 3). One possible explanation for this interesting finding is impairment of silane stability in the acidic environment.[74] Because the pH of UAs is 2.2 to 3.2 for self-etching capability, a self-condensation reaction occurs in the silanol groups of hydrolyzed silane.[75,76] Yoshihara *et al.* [77] analyzed the adhesive formulations using Fourier transform infrared spectrometry (FT-IR) and ^{13}C nuclear magnetic resonance (NMR). The commercial adhesive SBU, and the experimental adhesive formulations consisting of the SBU to which γ-

methacryloyl oxypropyl trimethoxysilane (γ-MTPS) was mixed, were analyzed using FT-IR and were analyzed immediately and 1 day after mixing using ^{13}C NMR. The strong peaks, representing the presence of silane, were only detected when the solutions were analyzed immediately after γ-MTPS was added using ^{13}C NMR, but they were not detected for the other samples using FT-IR and ^{13}C NMR. A second possible explanation is that Bis-GMA in SBU significantly inhibits the condensation reaction between the hydroxyl groups of LS2 ceramic and the silanol groups of silane.[78] Moreover, extra resin could also inhibit the condensation reaction that releases water molecules according to the Le Chatelier principle.[79] Another explanation is that the concentration of silane in SBU might not be sufficient to react with the hydroxyl groups of the ceramic surface. This was confirmed by the studies by Zaghloul *et al*.[78] and Kalavacharla *et al*.[26]. According to these authors, treatment with silane followed by SBU significantly improved the bond strength between the ceramic and the composite resin. The additional silanization step enhanced chemical bonding to the exposed hydroxyl groups and surface wettability with resin impregnation. In previous studies, this assumption was confirmed by the SEM images which were the fractured surfaces of SBU treated groups using IPS E.max CAD.[80] Discontinuity areas were observed on SBU layers, which meant an incomplete, intimate contact between SBU and resin cement. Furthermore, uncured HEMA lowers the vapor pressure of water and makes it difficult to remove water by air-drying.[81]

The results of the current study supported the importance of HF etching prior to ceramic surface bonding. Lower bond strength was obtained if the cement was applied without HF etching of the ceramic surface (Tables 3 and 5), which confirmed the findings reported in earlier studies.[13,50] The large difference in bond

strength contingent on HF etching is explained by the difference in surface texture (Figures 5a and 5c). HF etching of a ceramic surface dissolves the glass phase and forms soluble hexafluorosilicates, which can be rinsed out with water. In addition, HF etching creates surface irregularities, thus increasing surface area.[48] It also exposes OH groups, consequently improving the wettability of the ceramic by silane agents.

The application of HF etching, silane and adhesive showed the highest bond strength in comparison to other groups in both testing conditions using NX3 (Table 3). This procedure achieved durable bonds for silica-based ceramics.[11,82] Conversely, Isolan CP *et al.*[27] reported that the μSBS achieved with HF and SBU was higher than that obtained with HF, silane and Single Bond 2 (SB2, 3M ESPE) using feldspathic porcelain blocks. Although we used Porcelain Bonding Resin, which is HEMA-free, Isolan CP *et al.* used SB2, which contains HEMA. According to El Zohairy *et al.*[83] bonding agents containing hydrophilic monomers have a negative effect on resin-ceramic bonds. Therefore, HEMA in SB2 could adversely influence the bond strength during water storage. In addition, different experimental settings, such as the use of different ceramic blocks, could have influenced these results.

The bond strength of Group B, which was treated with silane and adhesive, was slightly higher compared to that of Group A, while it was significantly lower than that of Group C (Table 3). This indicated that silane contributes to the resin-ceramic bond, but showed that it is not sufficient to produce durable ceramic bonding without HF etching of the ceramic. This was corroborated by failure mode data, that is, adhesive failure was more common in Group B than in Group C.

ABU is composed of Bis-GMA, HEMA, and MDP. Further, SBU contains

silane and Vitrebond™ copolymer whose chemical structure is presented in Figure 7. The repeating unit of this copolymer has a double bond at the end of hydrocarbon chain and the double bonds are exposed to react with other monomers. Finally, it could form crosslinking. The three dimensional network of crosslinking increases mechanical properties (strength and rigidity) and decreases water sorption and solubility.[35] This is in agreement with the results obtained in the present study, as a statistically different in μSBS values was observed between Groups III and IV.

After 24-hour water storage, Group E (HF+SBU) showed slightly lower bond strength compared to Group C (HF+S+Ad), and Group III (HF+SBU) showed a similarly high level of bond strength to Group II (HF+S+Ad). However, application of both UAs yielded significantly lower bond strengths than HF, silane and adhesive treated groups after thermocycling (Tables 3 and 5), in accordance with previous studies.[28,80] Kalavacharla *et al*.[28] showed that additional silane application before SBU improved adhesion between resin cement and LS2 after thermocycling. Murill-Gomez *et al*.[80] concluded that a separate application of silane followed by an adhesive on etched LS2 showed better results than HF and SBU after 6 months of water storage. Those findings are similar with the data obtained in the present study. As mentioned above, an adhesive layer included HEMA could negatively influence the resin-ceramic bond durability,[83] and both UAs contain the hydrophilic monomer that vary from the monomers present in Ad (Table 7). The deterioration of the bond observed when UAs were used was correlated with the hydrophilic characteristics of the adhesives. Previous studies have proposed that water uptake will diminish the siloxane bond by hydrolysis and water swelling. HEMA has a low partition coefficient (P = 0.26). The more HEMA resin present, the more water is

absorbed.[84,85] The effect of swelling will stress the bond at the adhesive interface and will significantly weaken adhesive bonds.[83] This might also suggest that silane in SBU, which is unstable when combined with MDP and bis-GMA, and absence of silane in ABU compromised the long-term bonding.

Dental restorations are exposed to a harsh environment, such as repeated occlusal force, moisture and the thermal variation in the oral cavity. These can cause the failure of restorations. In the present study, thermal cycling was used to simulate clinical conditions. The post-thermocycling bond strength decreased significantly compared to baseline values of Groups B, C, E (Table 3), II, III and IV (Table 5). Several studies have proposed that thermocycling might have a negative effect on the bond strength between resins and ceramics.[67,86,87]

Two dual-cure resin cements were used in the present study. The degree of conversion positively correlates with mechanical properties in resin system.[88] Lührs, measured the degree of conversion using Raman spectrometer, showed that the higher degree of conversion observed for NX3 as compared with RXU.[89] The results of the present study was not corresponded to it. For HF and SBU-treated group, bonding with NX3 resulted in lower bond strength values than bonding with RXU after thermocycling (Figure 6). NX3 contains HEMA which could affect the bond durability above-mentioned. Beside, RXU contains various components (Table 1). One of them is '2-Propenoic acid, 2-methyl-1,1'-[1-(hydroxymethyl)-1,2-ethanediyl] ester, reaction products with 2-hydroxy-1,3-propanediyl dimethacrylate and phosphorus oxide (20-30%)', which may be a copolymer like Vitrebond™ copolymer. It could function as a rheological additive because the higher molecular weight polymer is, the higher viscosity has.[90] In addition, the monomers of copolymer contain two double bonds (Figure 8) which could react

with other monomers. The copolymer could possibly improve the physical properties of RXU to increase crosslinking density.

In current study, there were gaps in the resin-ceramic interface in Group E before thermocycling (Figure 5c) and spontaneous failure occurred in Group E during thermocycling for microscopic observation. Considering the composition of SBU and the gaps, the bond strength of Group E was significantly decreased after thermocycling. In contrast, the ceramic-adhesive-cement interface could not be detected and intimate bonding was observed in Group C before and after thermocycling (Figures 5b and 5d). This was consistent with the results of bond strength testing in Group C.

Weibull analysis provides failure probability as a function of stress and evaluates the overall performance of the bond within brittle materials.[91,92] In this study, the reliability and durability of the bond adhesion were investigated by comparison of Weibull parameters as well as comparing the mean bond strengths and standard deviations since the adhesive layer after polymerization is brittle.[72,93] The μSBS data fitted the Weibull distribution well, as shown by correlation coefficient (r) of over 0.9 for all groups (Tables 4 and 6).[94] According to definitions of the Weibull parameters, Weibull modulus (m) is a measure for the distribution of strength data. As characteristic bond strength (σ_θ) is a location parameter, it represents the strength responsible for 63.2% failed and is slightly greater than the mean bond strength value.[92,95] Low variability in the bond strengths will present a high m, which means high reliability of the characteristic bond strength. For the 24-hour water storage, the Weibull analysis showed a more reliable bond strength for Groups C, E, II, III and IV, which were treated with HF, as indicated by a higher Weibull moduli. Group B showed the highest Weibull modulus among non HF-

treated groups, that means silane attributes the bond between LS2 and resin cement. In HF, silane, and adhesive treated groups (Groups 3 and II), higher Weibull moduli and characteristic bond strength were found after thermocycling. It translates that this surface treatment could achieve reliable and durable bond to LS2.

The main limitation of this study is that few brand of UAs were tested. There are many UAs that have different compositions, as well as different ingredients (Table 7). For example, SBU and Clearfil Universal Bond (Kuraray Noritake Dental, Tokyo, Japan) include silane; other UAs were not incorporated silane. Some adhesives include special ingredients, such as 3-7% methacrylated carboxylic acid polymer in Adhese Universal (Ivoclar Vivadent), or 1-5% polyacrylic acid copolymer in SBU. Each UA may have different bonding interactions according to the surface treatments used and their ingredients. Further studies with adhesive and dual-cure resin cement contained MDP are needed because it is known that MDP was able to attribute to adhesive strength on non HF-treated lithium disilicate.[27]

VI. Conclusions

From the date of this experiments,

1. Surface treatment using UA itself could not form effective bond of resin cement to LS2. This means silane in UA did not work in terms of the bond between resin cement and LS2.

2. Regardless of the surface treatment procedure used, thermocycling significantly reduced the bond strength. After thermocycling, two UAs could not durably bond to LS2 compared to a separated use of silane and adhesive, though the surface was treated with HF.

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VIII. Figure legends

Figure 1. Experimental design of the study (a) Nexus3 (b) RelyX ultimate. HF, Hydrofluoric acid; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); SBU, Single Bond Universal; ABU, All Bond Universal.

Figure 2. Weibull curves of bond strength. (a) TC0, specimens after 24-hour water storage using Nexus3; (b) TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling using Nexus3; (c) TC0, specimens after 24-hour water storage using RelyX ultimate; (d) TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling using RelyX ultimate. *m*, Weibull modulus; σ_θ , the characteristic bond strength; HF, Hydrofluoric acid; S, silane; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); SBU, Single Bond Universal; ABU, All Bond Universal.

Figure 3. Distribution of failure mode after microshear bond strength testing. (a) Nexus3; (b) RelyX ultimate. TC0, specimens after 24-hour water storage; TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling.

Figure 4. Representative SEM photomicrographs of fractured ceramic surfaces after microshear bond strength testing showing (a) adhesive failure; (b) mixed failure; and (c) cohesive failure at 100X magnification. The arrow shows the fracture origin and the direction of the arrow represents that of shear force. In Figure (c), the resin cement remained on the loading point side. C, ceramic; Ad, adhesive; R, resin cement.

Figure 5. SEM micrographs of the fractured surfaces comparing the adaptation between the adhesive and the ceramic surfaces treated with different procedures: (a) Group B (silane [S], adhesive [Ad, Porcelain Bonding Resin, Bisco Inc.] and

resin cement [Nexus3, Kerr]) before thermocycling. The surface of the lithium disilicate was flat, and there was no micro-undercut, because hydrofluoric acid (HF) had not been applied. The Ad and resin cement layers can be discriminated. There were some filler particles in the adhesive layer. (b) Group C (HF, S, Ad and resin cement [Nexus3, Kerr]) before thermocycling. The borders of each material were not easily distinguishable because the Ad had infiltrated the micro-undercut and the fillers were distributed throughout the full thickness of the Ad. (c) Group E (HF, Single Bond Universal [SBU] and resin cement [Nexus3, Kerr]) before thermocycling. The etched ceramic surface had micro-undercuts and SBU had infiltrated the undercuts. However, there was a gap between the adhesive and the ceramic surface. (d) Group C (HF, S, Ad and resin cement [Nexus3, Kerr]) after thermocycling. This had a similar morphology to Figure 5b. Dashed arrow: the interface of the ceramic and adhesive; hollow arrow: the interface of the adhesive and resin cement; C, ceramic; Ad, adhesive; R, resin cement.

Figure 6. Mean microshear bond strength and standard deviation of experimental groups for comparing the effect of resin cements. (a) TC0; (b) TC10,000. HF, Hydrofluoric acid; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); SBU, Single Bond Universal.

*: statistically different ($p < 0.05$)

Figure 7. Chemical structure of Vitrebond™ copolymer in Single Bond Universal (3M ESPE).

Figure 8. Chemical structure of monomers in RelyX ultimate (3M ESPE) (a) 2-hydroxy-1,3- propanediyl dimethacrylate; (b) 2-propenoic acid, 2-methyl-1,1'-[1-(hydroxymethyl)-1,2-ethanediyl] ester.

Tables

Table 1. Materials used in the study (as provided by the manufacturers)

Product	Manufacturer	Main components	Lot number
E. max CAD	Ivoclar Vivadent, Schaan, Liechstein	Lithium disilicate	S51425
Ceramic etching gel	Ivoclar Vivadent, Schaan, Liechstein	5% Hydrofluoric acid	U48388
Bis-Silane	Bisco Inc., Schaumburg, IL, USA	Bottle A: Ethanol, 3-(trimethoxysilyl)propyl-2-methyl-2-propenoic acid Bottle B: Ethanol, silane	1500006136
Porcelain Bonding Resin	Bisco Inc., Schaumburg, IL, USA	Bis-GMA, UDMA, TEGDMA	1500003888
Single Bond Universal (SBU)	3M ESPE, St. Paul, MN, USA	Organophosphate monomer (MDP), Bis-GMA, HEMA, Vitrebond™ copolymer, filler, ethanol, water, initiators, silane	620316
All Bond Universal (ABU)	Bisco Inc., Schaumburg, IL, USA	Ethanol, Bis-GMA, HEMA, water, MDP	1600005252
Nexus3	Kerr, Orange, CA, USA	UDMA, TEGDMA, HEMA, pyridyl thiourea, cumene hydroperoixde, inert fillers, activators, stabilizers and radiopaque agent	5348829
RelyX ultimate (RXU)	3M ESPE, St. Paul, MN, USA	Base: silane treated glass powder, 2-propenoic acid, 2-methyl-1,1'-[1-(hydroxymethyl)-1,2-ethanediyl] ester, reaction products with 2-hydroxy-1,3-propanediyl dimethacrylate and phosphorus oxide, TEGDMA, silane treated silica, oxide glass chemicals, sodium persulfate, tert-butyl peroxy-3,5,5-triethylhexanoate, copper(II) acetate monohydrate Catalyst: silane treated glass powder, substituted dimethacrylate, 1,12-dodecane dimethycrylate, silane treated silica, 1-benzyl-5-phyenyl-barbic-acid, calcium salt, sodium p-toluenesulfinate, 2-propenoic acid, 2-methyl-,[(3-methoxypropyl)imino]di-2,1-ethanediyl ester, calcium hydroxide, titanium dioxide	604568
Filtek Z250	3M ESPE, St. Paul, MN, USA	Bis-GMA, UDMA, Bis-EMA, PEGDMA, TEGDMA, silane-treated ceramic	N596514

Bis-GMA, bisphenol A diglycidyl ether dimethacrylate; UDMA, urethane dimethacrylate; TEGDMA, triethylene glycol dimethacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; HEMA, 2-hydroxyethyl methacrylate; Bis-EMA, bisphenol A ethoxylate dimethacrylate; PEGDMA, polyethylene glycol dimethacrylate.

Table 2. Firing parameters of IPS E.max CAD (Ivoclar Vivadent, Schaan, Liechtenstein) for post-milling heat treatment.

Closing time	6 min
Stand-by temperature	403℃
Closing time	6 min
Heating rate	90℃/min
Firing temperature	820℃
Holding time	10 sec
Heating rate	30℃/min
Firing temperature	840℃
Holding time	7 min
Vacuum 1	550/820℃
Vacuum 2	820/840℃
Longterm cooling	700℃
Cooling rate	20℃/min

Table 3. Microshear bond strength after different surface treatments on lithium disilicate using Nexus3

Treatment groups	Bond strength (MPa)		Reduction rate of bond strength (%)
	TC0	TC10,000	
Group A Ad	1.80 ± 1.50 ^{Aa}	0.00 ± 0.00 ^{Ba}	100
Group B S+Ad	9.23 ± 3.45 ^{Ab}	3.03 ± 1.56 ^{Bb}	67.2
Group C HF+S+Ad	23.88 ± 8.42 ^{Ac}	13.67 ± 4.22 ^{Bc}	42.8
Group D SBU	2.04 ± 1.19 ^{Aa}	0.00 ± 0.00 ^{Ba}	100
Group E HF+SBU	19.50 ± 5.72 ^{Ad}	3.86 ± 2.34 ^{Bb}	80.2

Different superscript capitalized letters in the same row indicate a significant difference; different superscript lowercase letters in the same column indicate a significant difference.

Reduction rate of bond strength (%) = {(bond strength after 24-hour water storage – bond strength after thermocycling)/bond strength after 24-hour water storage} X 100

Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); HF, hydrofluoric acid; S, silane; SBU, Single Bond Universal.

Table 4. Weibull modulus (*m*) and characteristic bond strength (σ_0 in MPa) of the microshear bond strength values of the different surface treatment groups using Nexus3

Treatment groups	TC0 (*n* = 20)			TC 10,000 (*n* = 20)		
	m (90% CI)	σ_0 (90% CI)	r*	*m* (90% CI)	σ_0 (90% CI)	r*
Group A Ad	1.40 (1.21 - 1.58)	1.9 (0.2 – 4.2)	0.949			
Group B S+Ad	2.98 (2.68 – 3.28)	10.4 (3.80 – 15.0)	0.971	2.00 (1.74 – 2.25)	3.5 (0.8 – 6.0)	0.956
Group C HF+S+Ad	3.19 (2.97 – 3.40)	26.7 (10.5 – 37.7)	0.986	3.95 (3.53 – 4.37)	15.1(7.1 – 19.9)	0.968
Group D SBU	2.08 (1.86 – 2.31)	2.3 (0.6 – 3.9)	0.967			
Group E HF+SBU	3.77 (3.30 – 4.24)	21.7 (9.9 – 29.0)	0.957	2.01 (1.77 – 2.24)	4.3 (1.0 - 7.5)	0.962

Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); HF, hydrofluoric acid; S, silane; SBU, Single Bond Universal; CI, confidence interval.

*, Correlation coefficient.

Table 5. Microshear bond strength after different surface treatments on lithium disilicate using RelyX ultimate

Treatment groups	Bond strength (MPa)		Reduction rate of bond strength (%)
	TC0	TC10,000	
Group I Ad	2.44 ± 1.15^{Aa}	0.00 ± 0.00^{Ba}	100
Group II HF+S+Ad	22.78 ± 6.93^{Ab}	13.87 ± 4.06^{Bb}	39.1
Group III HF+SBU	23.50 ± 6.32^{Ab}	7.73 ± 3.56^{Bc}	67.1
Group IV HF+ABU	18.59 ± 5.31^{Ac}	3.98 ± 2.36^{Bd}	78.6

Different superscript capitalized letters in the same row indicate a significant difference; different superscript lowercase letters in the same column indicate a significant difference.

Reduction rate of bond strength (%) = {(bond strength after 24-hour water storage - bond strength after thermocycling)/bond strength after 24-hour water storage} X 100

Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); HF, hydrofluoric acid; S, silane; SBU, Single Bond Universal; ABU, All Bond Universal.

Table 6. Weibull modulus (*m*) and characteristic bond strength (σ_θ in MPa) of the microshear bond strength values of the different surface treatment groups using RelyX ultimate

Treatment groups	TC0 (*n* = 20)			TC 10,000 (*n* = 20)		
	m (90% CI)	σ_θ (90% CI)	r*	*m* (90% CI)	σ_θ (90% CI)	r*
Group I Ad	2.15 (2.04 – 2.26)	2.8 (0.7 – 4.6)	0.992			
Group II HF+S+Ad	3.91 (3.52 – 4.29)	25.2 (11.8 – 33.3)	0.972	3.66 (3.39 – 3.93)	15.4 (6.8 – 20.8)	0.984
Group III HF+SBU	3.38 (2.91 – 3.84)	26.5 (11.0 – 36.6)	0.948	2.29 (2.18 – 2.39)	8.8 (2.4 – 14.2)	0.994
Group IV HF+ABU	3.98 (3.55 – 4.42)	20.5 (9.7 – 27.1)	0.966	1.89 (1.70 – 2.08)	4.5 (0.9 – 8.0)	0.972

Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); HF, hydrofluoric acid; S, silane; SBU, Single Bond Universal; ABU, All Bond Universal; CI, confidence interval.

*, Correlation coefficient.

Table 7. Composition of adhesives according to the material safety data sheets provided by the manufacturers

	Porcelain Bonding Resin (wt%)	Single Bond Universal (wt%)	All Bond Universal (%)	Clearfil Universal Bond (%)	Adhese Universal (%)
Bis-GMA	< 40	15-20	20-50	15-35	20-<25
UDMA	< 40				
TEGDMA	< 30				
HEMA		15-20	5-25	10-35	20-<25
DGDMA		5-15			
Ethanol		10-15	30-50	<20	10-13
Water		10-15		+	
MDP		+	5-25	+	
Silane-treated silica		5-15			
Vitrebond™ copolymer		1-10			
Copolymer of acrylic and itaconic acid		1-5			
Dimethylaminobenzoate		<2			
(Dimethylamino) ethyl methacrylate		<2			
Methyl ethyl ketone		<0.5			
				Colloidal silica, silane	

Bis-GMA, bisphenol A glycidyl methacrylate; UDMA, urethane dimethacrylate; EGDMA, triethylene glycol dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; DGDMA, decamethylene glycol dimethacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate.

+: present, but composition information was not provided

Figures

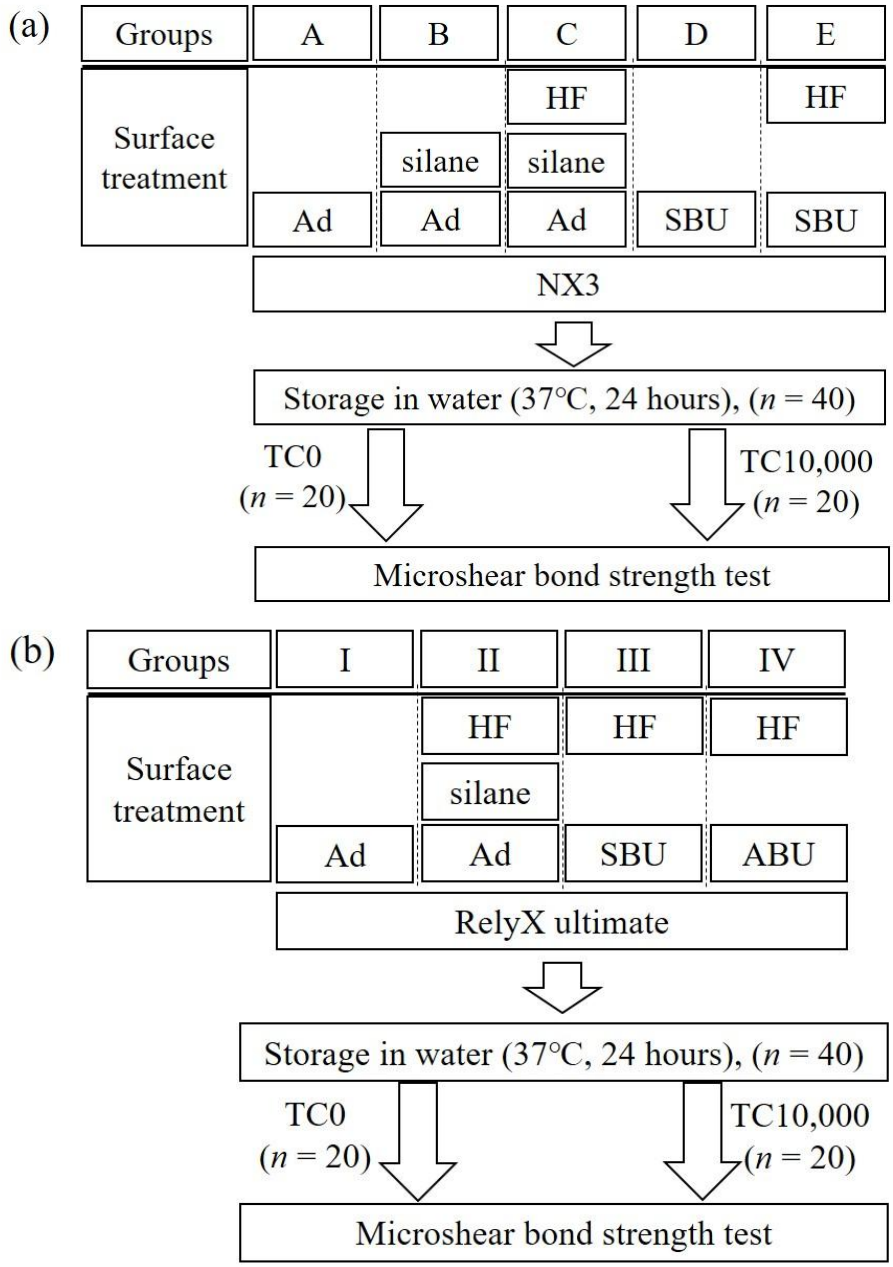


Figure 1. Experimental design of the study (a) Nexus3 (b) RelyX ultimate. HF, Hydrofluoric acid; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); SBU, Single Bond Universal; ABU, All Bond Universal.

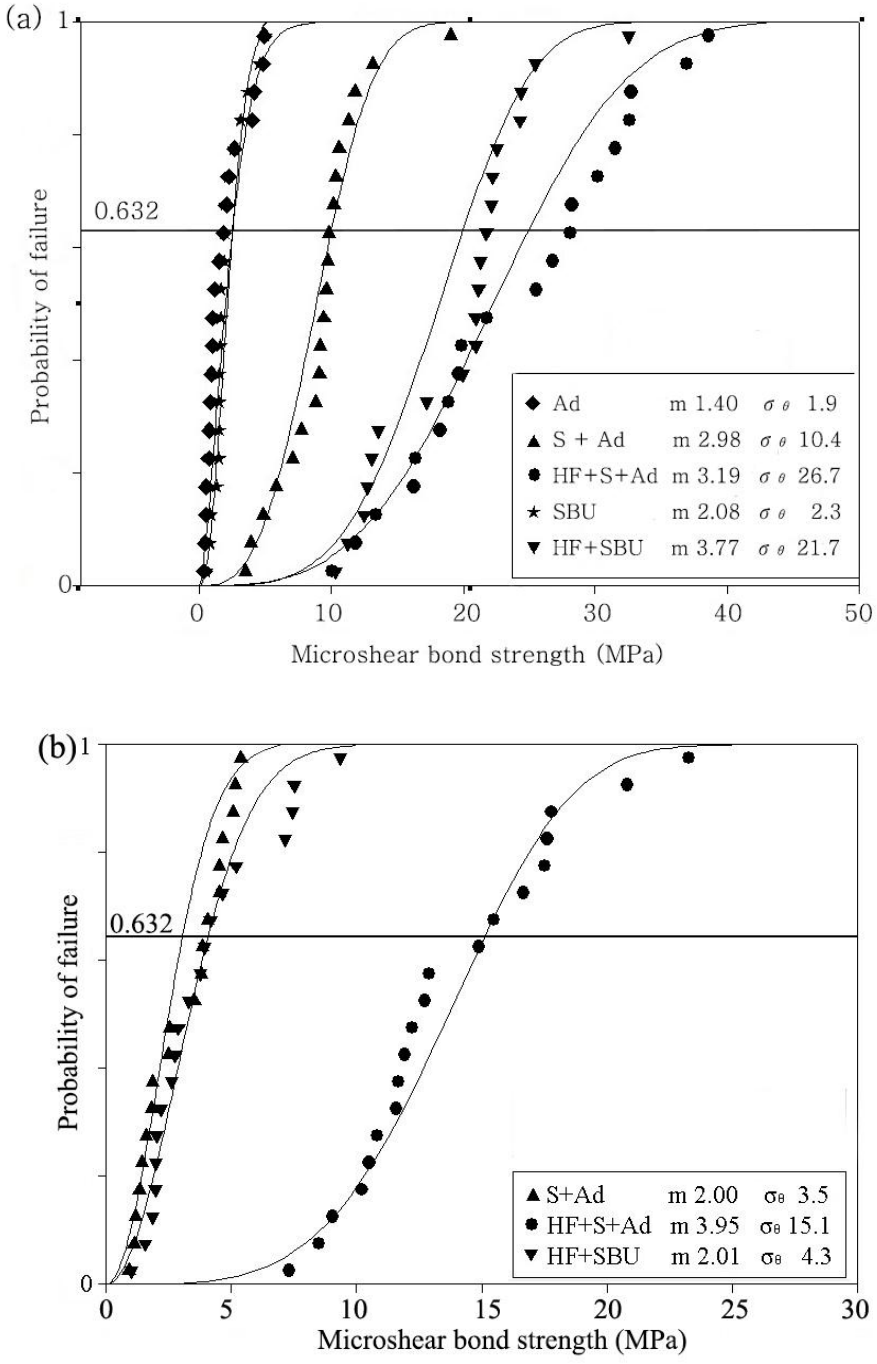
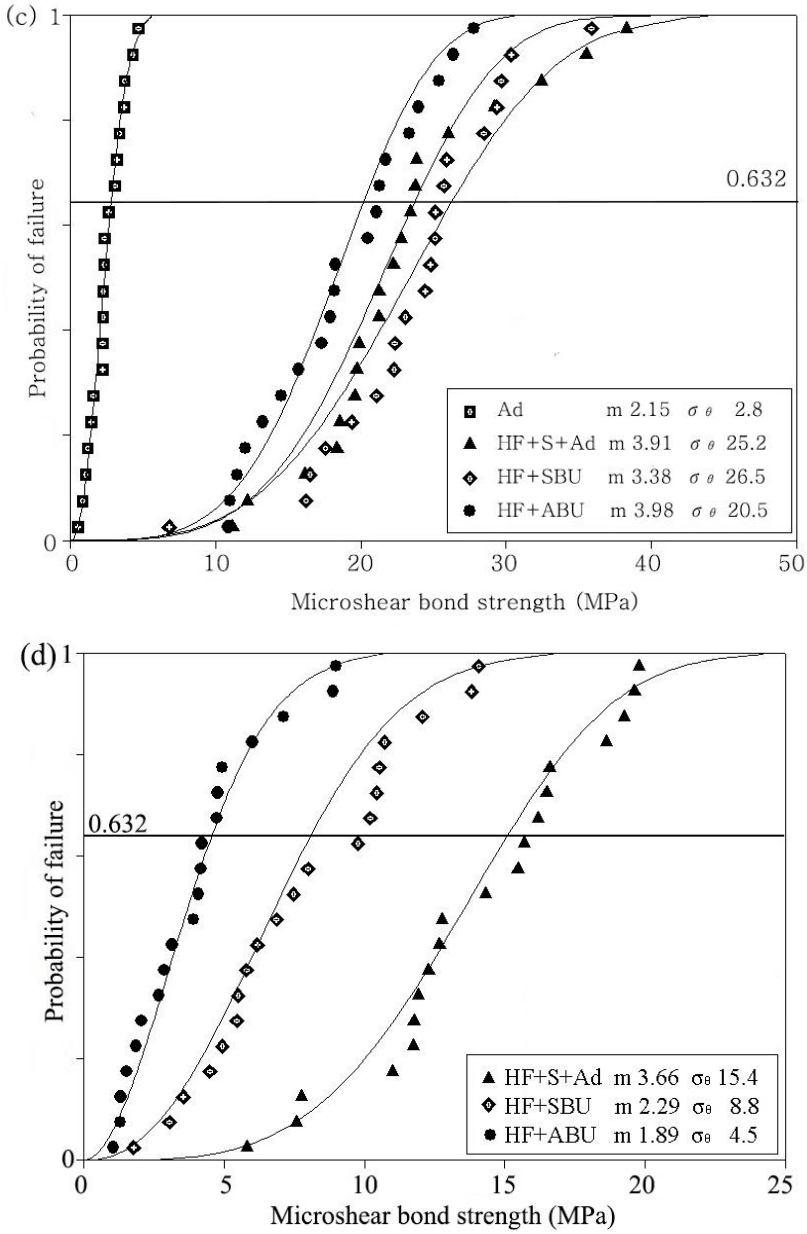
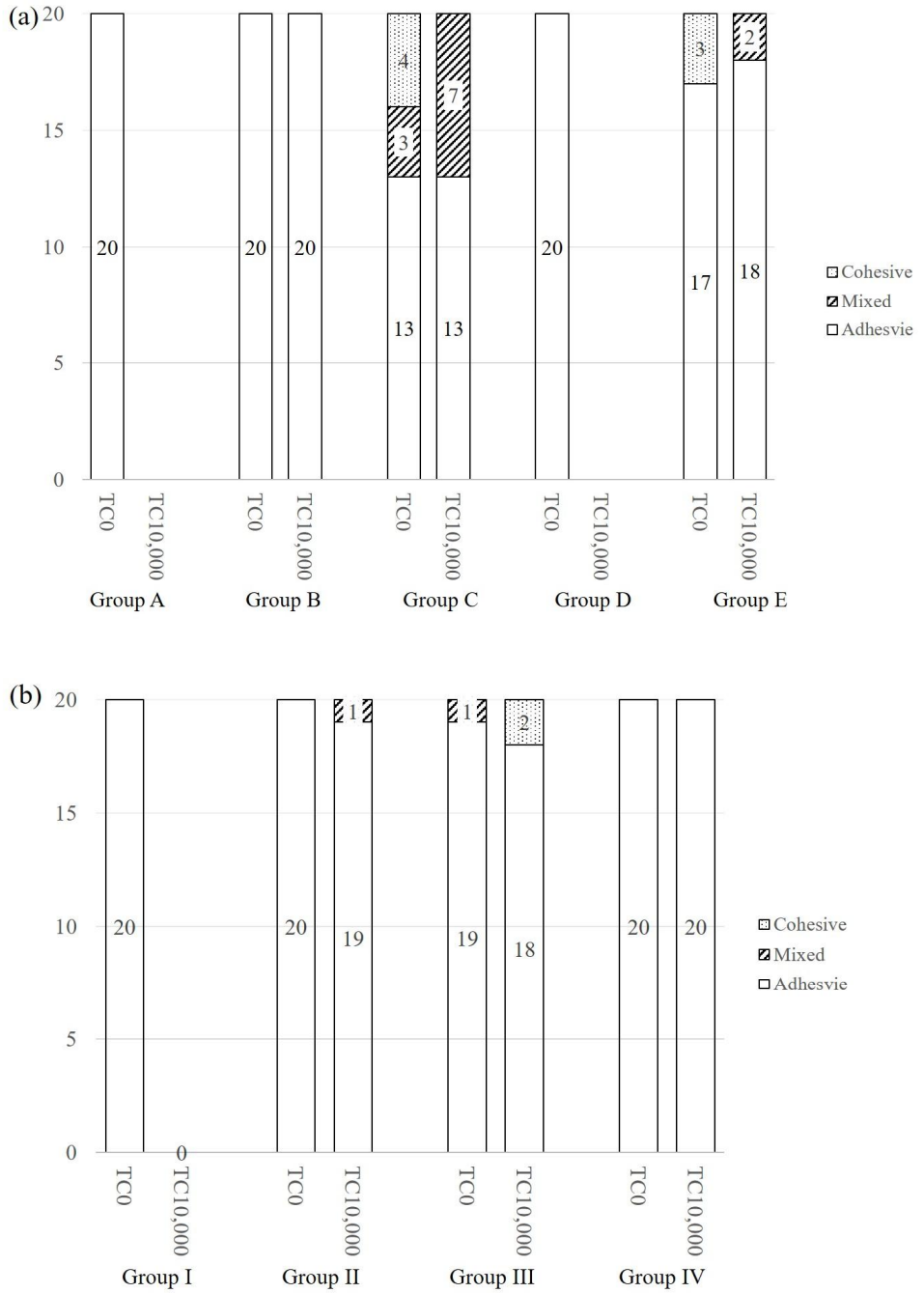


Figure 2. Weibull curves of bond strength. (a) TC0, specimens after 24-hour water storage using Nexus3; (b) TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling using Nexus3;



(Figure 2. continued) (c) TC0, specimens after 24-hour water storage using RelyX ultimate; (d) TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling using RelyX ultimate. *m*, Weibull modulus; σ_θ , the characteristic bond strength; HF, Hydrofluoric acid; S, silane; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); SBU, Single Bond Universal; ABU, All Bond Universal.



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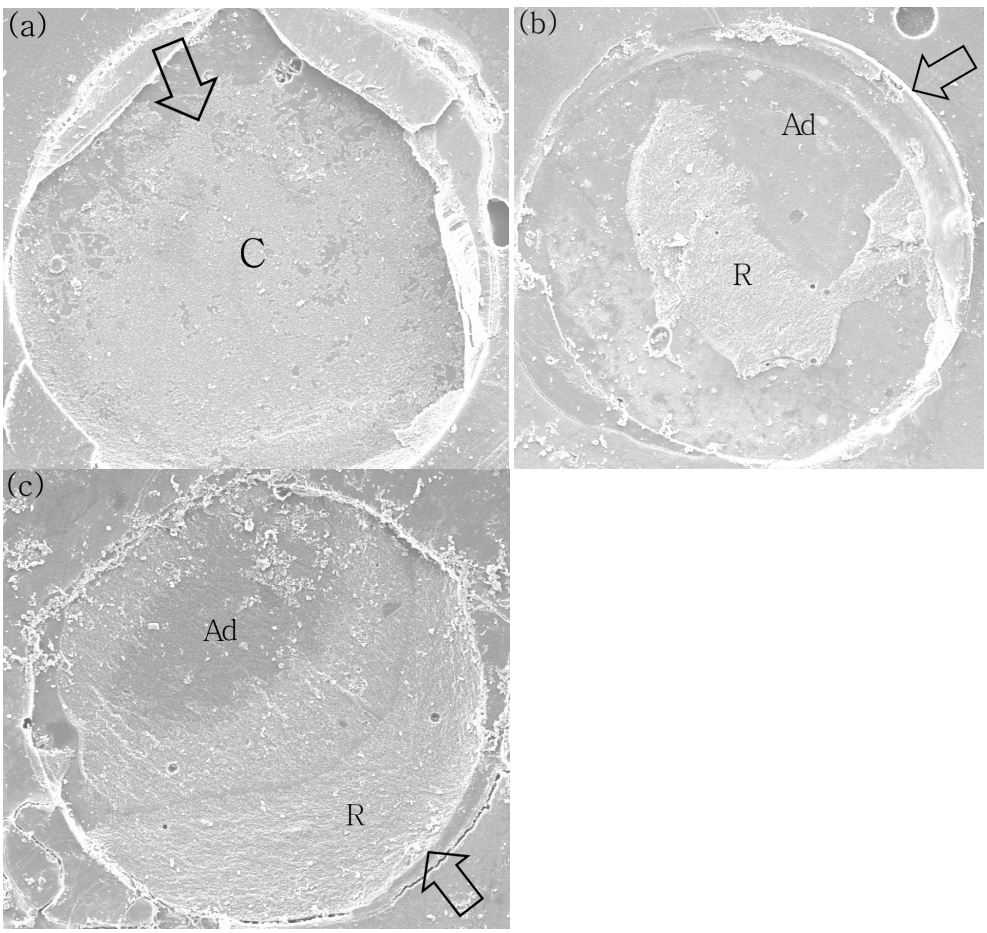

Figure 4. Representative SEM photomicrographs of fractured ceramic surfaces after microshear bond strength testing showing (a) adhesive failure; (b) mixed failure; and (c) cohesive failure at 100X magnification. The arrow shows the fracture origin and the direction of the arrow represents that of shear force. In Figure (c), the resin cement remained on the loading point side. C, ceramic; Ad, adhesive; R, resin cement.

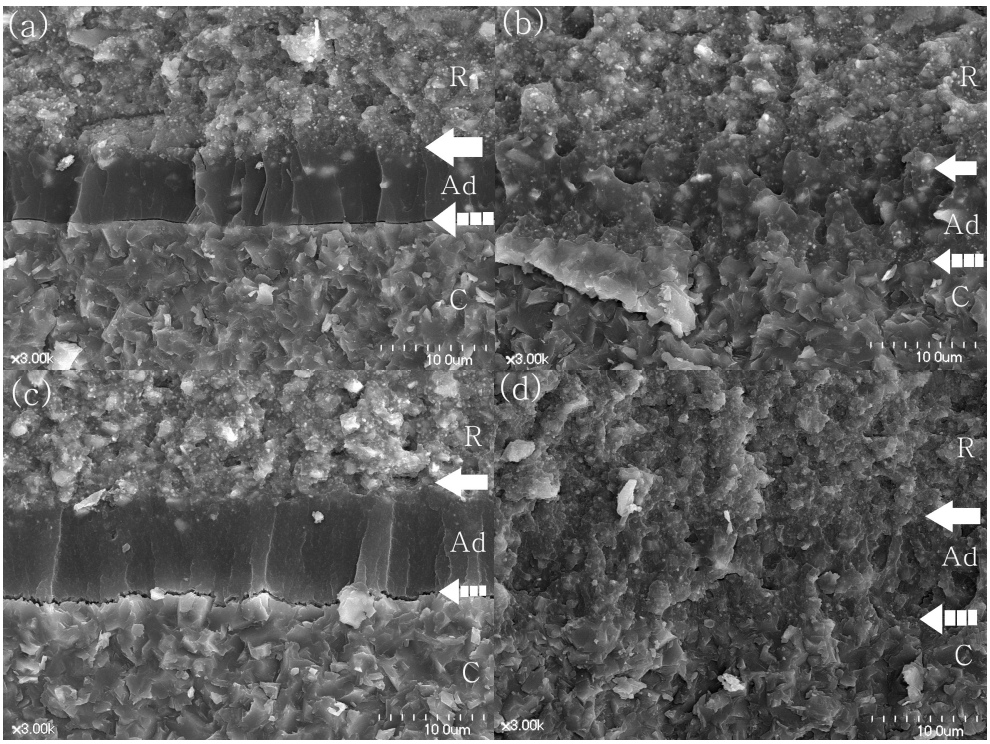

Figure 5. SEM micrographs of the fractured surfaces comparing the adaptation between the adhesive and the ceramic surfaces treated with different procedures: (a) Group B (silane [S], adhesive [Ad, Porcelain Bonding Resin, Bisco Inc.] and resin cement [Nexus3, Kerr]) before thermocycling. The surface of the lithium disilicate was flat, and there was no micro-undercut, because hydrofluoric acid (HF) had not been applied. The Ad and resin cement layers can be discriminated. There were some filler particles in the adhesive layer. (b) Group C (HF, S, Ad and resin cement [Nexus3, Kerr]) before thermocycling. The borders of each material were not easily distinguishable because the Ad had infiltrated the micro-undercut and the fillers were distributed throughout the full thickness of the Ad. (c) Group E (HF, Single Bond Universal [SBU] and resin cement [Nexus3, Kerr]) before thermocycling. The etched ceramic surface had micro-undercuts and SBU had infiltrated the undercuts. However, there was a gap between the adhesive and the ceramic surface. (d) Group C (HF, S, Ad and resin cement [Nexus3, Kerr]) after thermocycling. This had a similar morphology to Figure 5b. Dashed arrow: the interface of the ceramic and adhesive; hollow arrow: the interface of the adhesive and resin cement; C, ceramic; Ad, adhesive; R, resin cement.

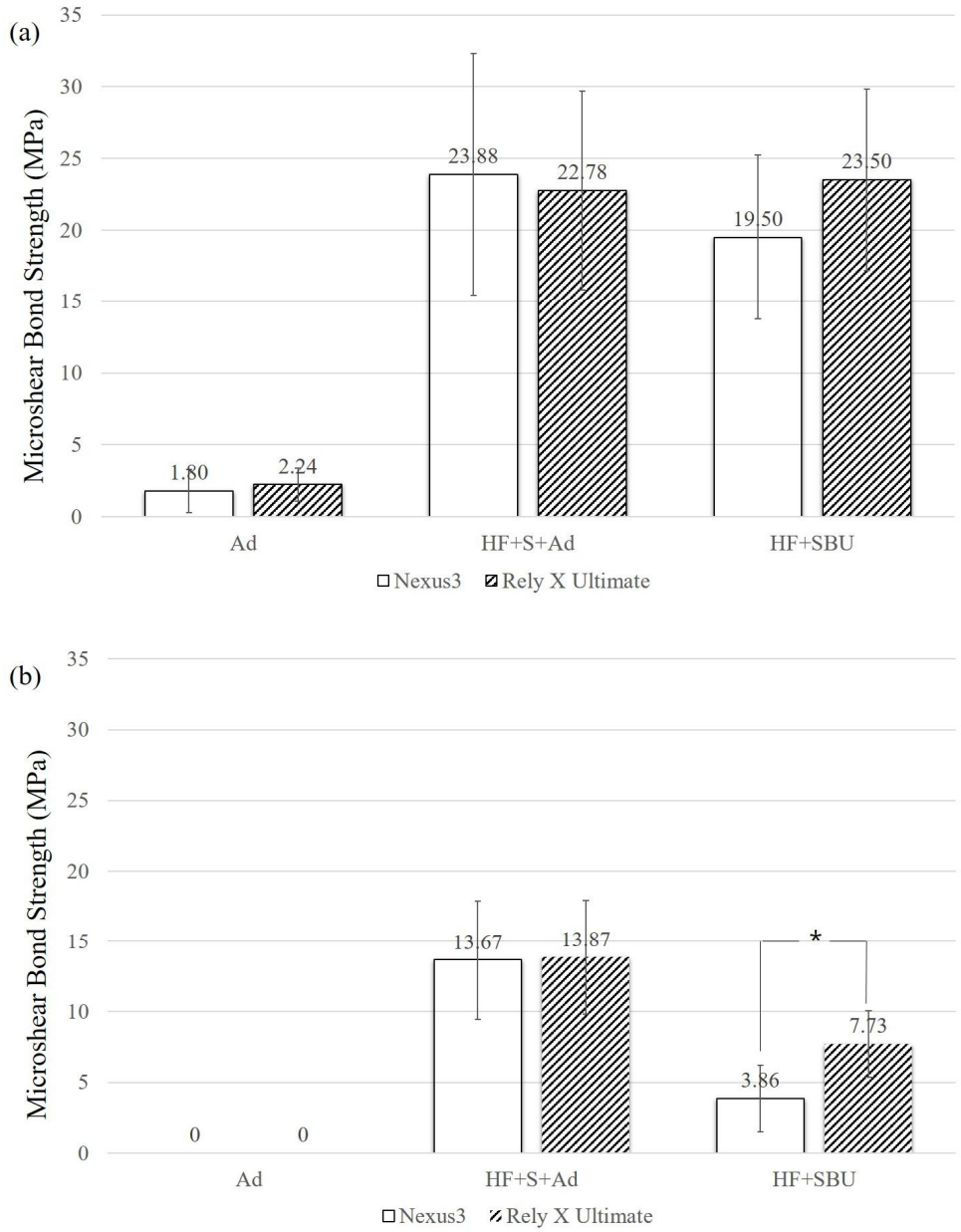

Figure 6. Mean microshear bond strength and standard deviation of experimental groups for comparing the effect of resin cements. (a) TC0, specimens after 24-hour water storage (b) TC10,000, specimens after 24-hour water storage and 10,000-cycle thermocycling. HF, Hydrofluoric acid; Ad, adhesive (Porcelain Bonding Resin, Bisco Inc.); S, silane; SBU, Single Bond Universal.

*: statistically different ($p < 0.05$)

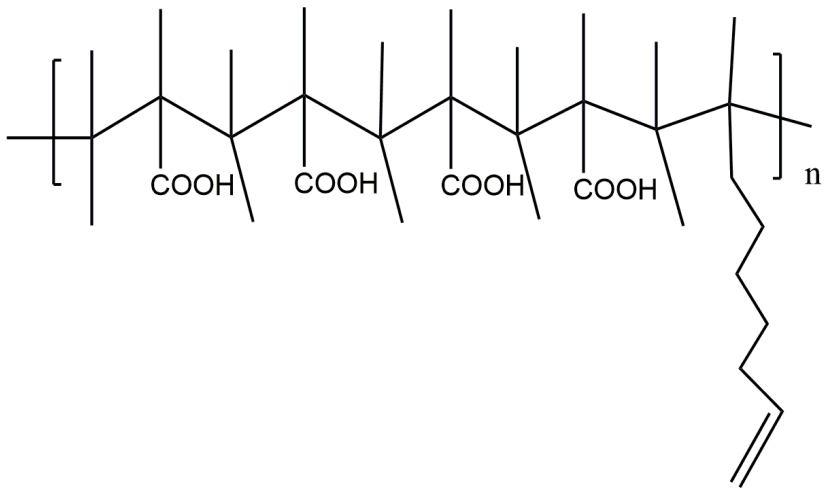

Figure 7. Chemical structure of Vitrebond^{TM} copolymer in Single Bond Universal (3M ESPE).

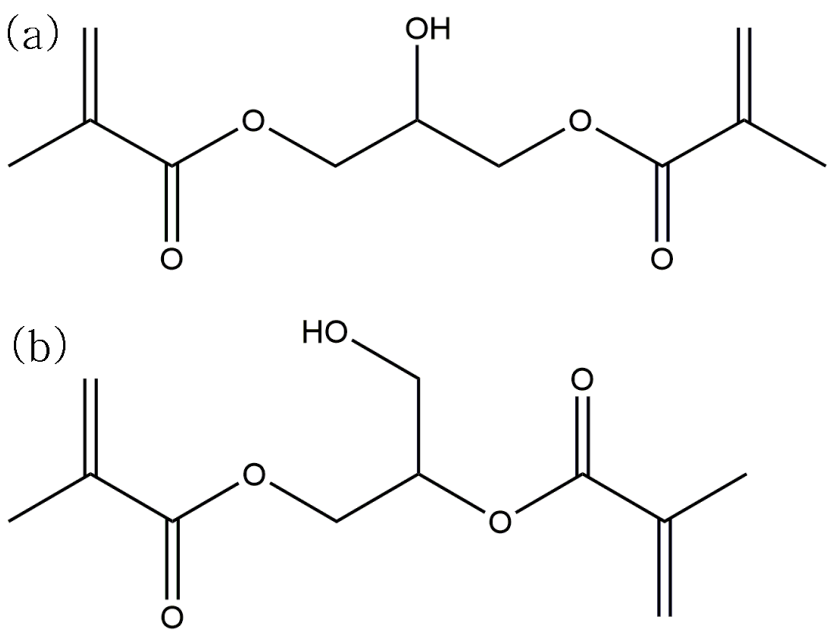

Figure 8. Chemical structure of monomers in RelyX ultimate (3M ESPE) (a) 2-hydroxy-1,3- propanediyl dimethacrylate; (b) 2-propenoic acid, 2-methyl-1,1'-[1-(hydroxymethyl)-1,2-ethanediyl] ester.

국문초록

리튬 다이실리케이트의 표면 처리 시 유니버설 접착제의 접착효과

이 현 영

서울대학교 대학원 치의과학과 치과보존학 전공

(지도교수 정 신 혜)

목적

본 연구의 목적은 리튬 다이실리케이트 (LS2)에 레진시멘트가 접착할 때 표면처리제로서 유니버설 접착제가 미치는 영향을 미세전단접착강도를 이용하여 평가하고자 하였다.

재료 및 방법

본 연구에서 두 종류의 아민을 포함하지 않은 레진시멘트 (Nexus3 [NX3, Kerr], RelyX ultimate [RXU, 3M ESPE])를 사용하였다.

직사각형 판 형태로 IPS e.max CAD (Ivoclar Vivadent) 시편 72개를 준비하고 다음과 같이 표면을 처리한다.

NX3 레진시멘트를 사용한 경우 표면처리는 다음과 같다. Group A, 접착제 (Ad, Porcelain Bonding Resin, Bisco Inc.); Group B, 실레인 (S, Bis-Silane, Bisco Inc.)과 Ad; Group C, 5% 불산 (HF, Ceramic Etching Gel, Ivoclar Vivadent), S와 Ad; Group D, Single Bond Universal (SBU, 3M ESPE); Group E, HF와 SBU. NX3 이중중합 레진시멘트를 적용한다.

RXU 레진시멘트를 사용한 경우 표면처리는 다음과 같다. Group I, Ad; Group II, HF, S와 Ad; Group III, HF와 SBU; Group IV, HF와 All Bond Universal (ABU, Bisco Inc.). RXU 이중중합 레진시멘트를 적용한다.

미리 제작된 지름 0.8 mm 컴포지트 (Filtek Z250, 3M ESPE) 레진 원기둥 (n = 40)을 시편 표면에 올리고 40 초간 광중합을 시행한다. 접착된 시편을 24시간 물에 보관한다. 시편의 절반 (n = 20)은 10,000회 열순환처리를 시행한다. 모든 시편들에 미세전단접착강도 시험을 시행한다. 접착강도 데이터는 다변량 분산 분석과 Tukey HSD 사후분석을 시행한다 ($p < 0.05$). 두 레진시멘트가 접착에 미치는 영향을 보기 위하여 삼원변량 분산 분석을 시행한다 ($p < 0.05$).

결과

NX3 레진시멘트를 사용한 경우 A와 D군을 제외한 나머지 군들의 접착강도 사이에서 유의한 차이를 보였다 ($p < 0.05$). 초기 접착강도는 C군 (23.88 MPa)이 가장 높았으며 이어서 E군 (19.50 MPa), B군 (9.23 MPa), D군 (2.04 MPa), A군 (1.80 MPa)순으로 높았다. 열순환처리는 B, C, E군의 접착강도를 감소시켰다 ($p < 0.05$). C군에서 실험 조건과 관계없이 가장 높은 접착강도를 보였다 ($p < 0.05$).

RXU 레진시멘트를 사용했을 때, 열순환처리 전에는 III군 (23.50 MPa)과 II군 (22.78 MPa)은 유사한 접착강도를 보였으며 ($p > 0.05$), IV군 (18.59 MPa)보다 높았다 ($p < 0.05$). I군의 접착강도는 나머지군들(II, III, IV)의 접착강도보다 유의하게 낮았다 ($p < 0.05$). 열순환처리 후, 모든 군에서 접착

강도는 감소하였다. 그 중에서 II군이 가장 높은 접착강도를 보였다 ($p < 0.05$).

이중중합 레진시멘트가 접착에 미치는 영향을 살펴보면, 세라믹 표면을 HF와 SBU로 처리하고 열순환처리한 경우 RXU가 NX3보다 높은 접착강도를 보였으며 ($p < 0.05$), 다른 군에서는 두 시멘트간 유의한 차이가 없었다.

결론

본 실험의 결과들을 종합하면, 유니버설 접착제로 LS2 표면을 처리했을 때 레진시멘트가 효과적인 접착을 형성하지 못하였다. 열순환처리 후 결과를 비교하면, 불산으로 LS2 표면을 처리하였음에도 불구하고 두 유니버설 접착제를 적용한 경우가 개별적으로 실레인과 접착제를 적용했을 때보다 결합 내구성이 감소하였다.

주요어 : 리튬 다이실리케이트, 유니버설 접착제, 미세전단접착강도, 레진시멘트, 실레인, 열순환처리

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